

Experimental Studies of the Phase Relations in the System Fe-O at High Pressures

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Introduction: Wüstite is an iron oxide that possesses rock-salt structure and exhibits a wide range of nonstoichiometry ($0.88 < x < 1$ in Fe_xO). At atmospheric pressure, this oxide is thermodynamically stable at temperatures above 849 K, whereas at lower temperatures it disproportionates to magnetite plus metallic iron. The stoichiometry of wüstite is defined by two univariants, one for wüstite in equilibrium iron, the other in equilibrium with magnetite, with the eutectoid point at 849 K and $x \approx 0.945$ in the temperature-composition space. The phase relations in the system Fe-O at high pressures have been investigated by a number of authors, both experimentally and theoretically¹. Our understanding on this issue, however, is far from complete. The precise values of the eutectoidal temperature and composition at high pressure, for example, have not been determined by any previous experiment. While several studies have aimed at determining the wüstite/iron phase boundary², the effect of pressure on the wüstite/magnetite (i.e., oxygen-rich) phase boundary is entirely not known, even though some insights can be inferred from the only available experimental study of Shen et al.³ In the absence of these critical information, it would be difficult to evaluate the reliability of the phase relations derived from thermodynamic calculations. In the present work, the wüstite/magnetite phase boundary and the eutectoidal temperature and composition in the system Fe-O are determined at four different pressures based on in-situ observations and volume measurements at high temperature.

Methods and Materials: The starting wüstite was prepared by heating Fe_2O_3 to 1200°C under controlled oxygen fugacity ($f_{\text{O}_2} = 10^{-11.9}$ atm) in a CO-CO₂ gas-mixing furnace. The lattice parameter of this synthesized sample is $a_0 = 4.309(1)$ Å, corresponding to composition $\text{Fe}_{0.945}\text{O}$. An energy-dispersive X-ray method was employed using white radiation from the superconducting wiggler magnet at Beamline X17B of the National Synchrotron Light Source. The incident X-ray beam was collimated to dimensions of 100×200 μm, and diffracted X-rays were collected by a solid-state Ge detector at fixed angles of 2θ . Pressure was determined by EOS of NaCl and temperature by a W-Re thermocouple. In each experiment, the sample was first compressed at room temperature to the targeted pressure, followed by heating to the temperature of 1073 K. During heating, the pressure decreased due to relaxation of deviatoric stress (Weidner et al., 1992), and the x-ray diffraction data were collected along this path at steps of 50-100 K. On cooling, the pressure was controlled to be constant within 0.1 GPa of the desired values at each temperature condition, and the data were collected at steps of 50-100 K.

Results: Upon heating at 2.2, 3.1, and 6.3 GPa, exsolution of magnetite was first observed at 523-573 K. Since no iron metal (bcc or fcc phase) was observed in the diffraction patterns for all experiments reported here, the observed processes must follow a kinetically-controlled reaction $\text{Fe}_x\text{O} \rightarrow \text{Fe}_y\text{O} + \text{Fe}_3\text{O}_4$, with $y > x$. Magnetite was found to coexist with wüstite up to 823-873 K, but its relative intensity started decreasing at 723 K. At 873 K and higher temperatures, wüstite became the only stable phase at all three pressures. During cooling from 1073 K, the process was reversible and magnetite exsolution reoccurred at 673-723 K. The relative intensity of magnetite increased dramatically from 723 to 673 K, whereas at lower temperatures it remained constant. The wüstite + magnetite assemblage retained to room-temperature on further cooling and was recovered at ambient conditions. Because of the magnetite exsolution, the lattice parameters and hence stoichiometries of the coexisting wüstite show a number of discontinuous variations with temperature on both heating and cooling, and the temperatures of the discontinuities are tightly constrained by the present experiments. In the experiment at 8-9.5 GPa, however, magnetite was not observed on both heating and cooling in the range 300-1073 K. As a result, the unit-cell volume of wüstite show smooth variation with temperature, and the composition of the recovered sample is similar to that of the starting wüstite. These information make it possible to construct the temperature-composition (T-x) phase diagram for the Fe-O system.

Conclusions: In this study, the phase relations in the system Fe-O have been studied at 1.9, 2.7, 5.4 and 8.2 GPa from synchrotron x-ray experiments. The eutectoid temperature was found to decrease substantially with pressure; at 1.9 GPa, for example, the eutectoid temperature is determined to be 673 K. The eutectoid composition was found to shift from $x = 0.95$ at ambient pressure to higher iron content (i.e., $x = 0.99$) at high pressures. The field of wüstite expands with pressure as a result of diminishing field for wüstite + magnetite assemblage at 8-9 GPa.

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References: ¹ S. Stolen, J. Geophys. Res., 101, 11531 (1996). ² C.A. McCammon, Science 259, 66 (1993). ³ P. Shen, W.A. Bassett, and L. Liu, Geochim. Cosmochim. 47, 773 (1983).